

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 October 2002 (24.10.2002)

PCT

(10) International Publication Number
WO 02/083998 A1

(51) International Patent Classification⁷: **C30B 35/00**

(21) International Application Number: PCT/US02/09463

(22) International Filing Date: 25 March 2002 (25.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2001111055 16 April 2001 (16.04.2001) RU

(71) Applicant: **CORNING INCORPORATED** [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US).

(72) Inventors: **GARIBIN, Evgeny A**; Rybatsky pr., d.45, korp.1.kv.28, 193036 Saint Petersburg (RU). **DEMI-DENKO, Aleksay A**; ul. Pribrezhnaya, d.4, kv.39, 193076 Saint Petersburg (RU). **KVASHNIN, Boris I**; pr. Stachek, d.1, kv.36, 198095 Saint Petersburg (RU). **MIRONOV, Igor A**; Maly pr. PS, d.20, kv.19, 197042 Saint Petersburg (RU). **PETROVSKY, Gury T**; ul.Bolotnaya.d.14, kv.4,

194021 Saint Petersburg (RU). **REYTEROV, Vladimir M**; ul. Babushkina, d.36, kv.85, 193171 Saint Petersburg (RU). **SINEV, Aleksandr N**; ul.Shotmana, d.11, kv.84, 193232 Saint Petersburg (RU).

(74) Agent: **MURPHY, Edward F**; Corning Incorporated, SP TI 3 1, Corning, NY 14831 (US).

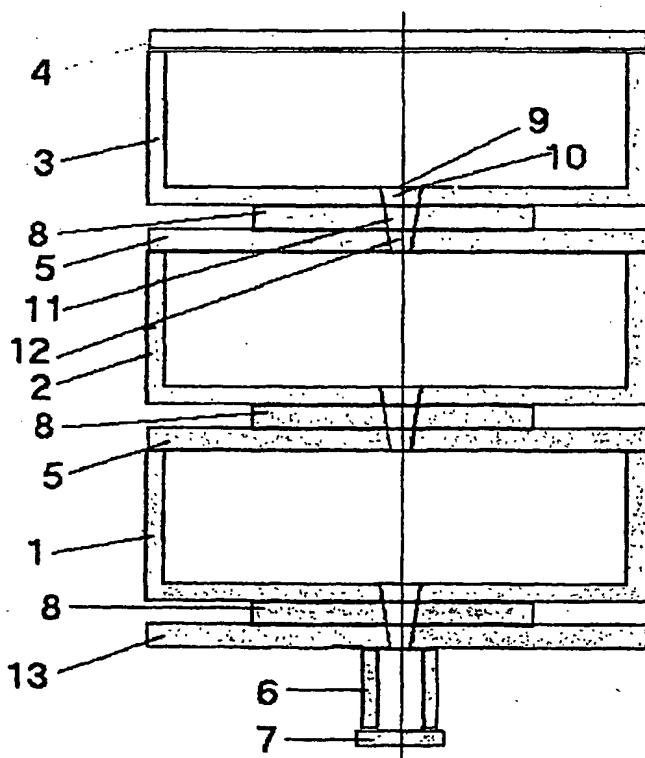
(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

Published:
— with international search report

[Continued on next page]

(54) Title: MULTICOMPARTMENT CONTAINER FOR GROWING CALCIUM FLUORIDE MONOCRYSTALS



(57) Abstract: The invention provides a method of making UV < 200 nm transmitting optical fluoride crystals for excimer laser lithography optics and a multicompartment container for growing optical fluoride crystals, comprising a number of graphite bowls (1, 2, 3) that are placed on top of one another to form a stack and which have a central conical orifice (10, 11, 12) in the bottom of each of them, and also comprising a seeding unit (6) that has a central cylindrical orifice (19, 11, 12) and is arranged under the lowermost bowl (1), characterized in that each bowl is fitted with a heat-removing device (8) that is made in the form of a graphite cylinder with a central conical orifice (10, 11, 12), is mounted under the bottom of each bowl, and adjoins, with its other surface, the cover of the next bowl down, in which design the cover of each bowl, apart from the uppermost one (3), has a central conical orifice (10, 11, 12).

WO 02/083998 A1

To grow the crystals in such crucibles, the whole stack of vessels is transferred, inside the crystallization furnace, from the melting zone to a zone where the temperature is kept below the crystallization temperature. The crystals growth begins in the lowest vessel and continues upward in each of the higher ones, as they successively traverse the crystallization isotherm (see pp. 106 and 107 in the Russian book entitled "Opticheskiy flyuorit" [Optical-Grade Fluorite] by N. P. Yushkin et al., published by Nauka in Moscow in 1983).

An example of the multicompartment crucible is represented by the apparatus described in a Japanese Patent Application entitled "Preparation of Calcium Fluoride Crystals" (see Japanese Patent Application No. 136515 of the Heisei Era 1.8 (1996), dated May 30, 1996 and published on December 9, 1997 / Japanese Patent Application – Kokei Series – No. 315893 of the Heisei Era 1.9 (1997)). In the apparatus described there, the stack consists of a set of bowls placed on top of one another. Each of these bowls is filled with the charge independently, and the bowls do not communicate with one another. The crystal growth occurs in each bowl separately, and independently of the process taking place in the other bowls.

In the prior-art apparatus that is the most like the object of the present invention is one comprising a "multistory" crucible, in which disk-shaped fluorite crystals are used as intermediate products for further growth (see p. 107 in the book "Optical Fluorite" by Yushkin et al., mentioned above). Each cavity (bowl) in this crucible has at its bottom a conical orifice to allow the melt to flow through from the higher cavity to the lower one, but this orifice is closed in the lowermost bowl.

During the crystallization of the melt, a penetrative growth (intergrowth) takes place through the orifice in the bottom of each bowl, and the small monocrystals thus formed serve as nuclei for the formation of monocrystalline intermediates in the cavities of the upper mold. The chances of a spontaneous formation of a crystal nucleus are practically nil here.

The main problem encountered in the preparation of crystals in the known apparatuses relates to the difficulty of obtaining high-quality optical-

grade crystals that have a fixed crystallographic orientation, a low birefringence and a high optical uniformity. A rigorous crystallization regime or system must be used to make this preparation possible. The temperature domain must be so structures as to ensure the absence of any temperature gradients in the charge-melting zone, which guaranteeing a steep temperature gradient in the crystallization zone, and again none in the annealing zone.

In the prior art that is the most like the object of the present invention, the temperature domain with its special structure is created by heaters and a set of reflecting shields used to remove the heat. However, these means do not make it possible to obtain crystals that have the required orientation and a birefringence of less than 5-10 nm/cm.

SUMMARY OF THE INVENTION

An aspect of the present invention is to prepare calcium fluoride monocrystals that are oriented in a fixed crystallographic direction and have a low birefringence (less than 5 nm/cm) and a high optical uniformity, by means of a preferred additional removal of heat from the center of crystal formation.

An aspect of the invention is achieved by an improved construction of the multicompartment container, which consists of a) a number of graphite bowls, placed on top of one another, each of which is fitted with a central conical orifice in its bottom part, and b) a seeding until that has a central cylindrical orifice and is mounted under the bottom of the lowermost bowl. Unlike in the most similar prior art, each bowl of the container is fitted here with a heat-removing device in the form of a graphite cylinder. Each of these cylinders has a central conical orifice, is mounted under the bottom of each bowl, and adjoins, with its other surface, a flat piece that has a central conical orifice and serves as the cover or lid for the next bowl down.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a multicompartment crucible container in accordance with the invention.

Fig. 2 shows a crucible container in accordance with the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference will now be made in detail to the present preferred embodiments of the invention.

The diameter of the graphite cylinder is 0.5-0.7 times the diameter of the bottom of the bowl, and its height is 0.5-1.0 times the thickness of the bottom of the bowl, and the thickness of the cover or lid is 1.0-1.5 times the thickness of the bottom of the bowl. The conical orifices that are formed in the bottom of the bowls, in the graphite cylinders of the heat-removing devices, and in the covers can all be connected together to form a common conical orifice with an angle of taper of 10-20° and a diameter of 3-5 mm in its lower part.

The heat-removing device may form a single unit with the bottom of the corresponding bowl and with the cover of the next bowl down.

The seeding unit is closed with a stopper at the bottom.

In a preferred embodiment, the construction of the heat-removing unit guarantees the required ideal removal of the heat from the central part of the bottom of each bowl in an axial direction throughout the crystal-growing period, and this creates favorable conditions for growing monocrystals, relieving their internal stresses, and improving their uniformity.

The dimensions of the graphite cylinder of the heat-removing device and the cover of the bowl below are chosen so as to ensure the best parameters for the gradients of the temperature domain, in which the crystallization front of the growing crystal is planar or only slightly convex. A crystallization front having this shape minimizes the radial gradients in the growing crystal, as a result of which the stresses and deformations of the crystal lattice are also minimized.

Fig. 1 shows a diagram of the multicompartment container, where:

BEST AVAILABLE COPY

- 1 is the lowermost bowl
- 2...-n are the successive bowls placed on top of one another to form a stack on the lowermost bowl (the number of these bowls may vary)
- 3 is the uppermost bowl, closed at the top with a cover
- 4 and
- 5 are the covers of the bowls below the top one
- 6 is the seeding unit
- 7 is the stopper closing the seeding unit at its bottom
- 8 is the heat-removing device in the form of a graphite cylinder
- 9 is a conical orifice formed by parts 10, 11 and 12, between the cavities of the bowls
- 10 is the central orifice in the bottom of each bowl
- 11 is the central orifice of the graphite cylinder 8
- 12 is the central orifice in the cover of each bowl, apart from the top one
- 13 is an optional extra component in the form of a flat piece that may be arranged under the bottom bowl and which has the same structure as the cover of the other bowls.

Fig. 2 shows one of the bowls of the container, which bowl is constructed so as to form a single unit with the heat-removing device 8 and with the cover 5 or the flat piece 13 mounted below the bowl. The resulting joint conical orifice has a diameter of 3-5 mm in its lower part, and an angle of taper of 10-20°.

All the bowls are made with the same dimensions, and the following relations hold for the various diameters:

$$d = (0.5-0.7) \cdot D$$

$$h_2 = (0.5-1.0) \cdot h_1$$

$$h_3 = (1.0-1.5) \cdot h_1$$

where

h_1 is the thickness of the bottom bowl

h_2 is the height of the heat-removing cylinder 8

h_3 is the thickness of the cover of each bowl

D is the outside diameter of the bottom of the bowl, and

d is the outside diameter of the heat-removing cylinder 8.

All the parts of the container construction are made of graphite.

The technological process of growing crystals is carried out as follows.

The nucleus, which is a crystal of the material to be grown and has the required orientation, is placed in the seeding unit 6, which the charge, consisting of the crystals to be grown, is placed in the bowls 1, 2 and 3. The container is introduced into the crystal-growing furnace, and the chamber of the furnace is evacuated to a residual pressure of at least 5×10^{-5} mm Hg. The furnace is heated to the temperature at which the charge melts, and the container is then moved from the upper, hot zone to the lower, colder zone of the chamber of the furnace, whereby the melt undergoes crystallization.

This process gave calcium fluoride monocrystals with a diameter of 300 mm, a thickness of 70 mm, an optical uniformity of $(1-3) \times 10^{-6}$ and a birefringence of 1-3 nm/cm.

It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit and scope of the invention. Thus it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

Claims:

1. A multicompartment container for growing calcium fluoride crystals, comprising a number of graphite bowls that are placed on top of one another to form a stack and which have a central conical orifice in the bottom of each of them, and also comprising a seeding unit that has a central cylindrical orifice and is arranged under the lowermost bowl, characterized in that each bowl is fitted with a heat-removing device that is made in the form of a graphite cylinder with a central conical orifice, is mounted under the bottom of each bowl, and adjoins, with its other surface, the cover of the next bowl down, in which design the cover of each bowl, apart from the uppermost one, has a central conical orifice.
2. A multicompartment container according to claim 1, characterized in that the outside diameter of the graphite cylinder is 0.5-0.7 times the diameter of the bottom of the bowl, the height of the graphite cylinder is 0.5-1.0 times the thickness of the bottom of the bowl, the thickness of the cover of each of the lower bows is 1.0-1.5 times the thickness of the bottom of the uppermost bowl, and the conical orifices of all the parts that can be connected together form a smooth passage with an angle of taper of 10-20°, the diameter of the cone in its lower part being 3-5 mm.
3. Multicompartment container according to claim 1 or 2, characterized in that the heat-removing device forms a single unit with the bottom of the bowl and the cover of the next bowl down.
4. A multicompartment container for growing optical fluoride crystals, comprising a number of graphite bowls that are placed on top of one another to form a stack and which have a central conical orifice in the bottom of each of them, and also comprising a seeding unit that has a central cylindrical orifice and is arranged under the lowermost bowl, and each bowl is fitted with a heat-removing device that is made in the form of a graphite cylinder with a

central conical orifice, and is mounted under the bottom of each bowl, and adjoins, with its other surface, the cover of the next bowl down, and in which the cover of each bowl, apart from the uppermost one, has a central conical orifice.

5. A multicompartment container according to claim 4, wherein the outside diameter of the graphite cylinder is 0.5-0.7 times the diameter of the bottom of the bowl, the height of the graphite cylinder is 0.5-1.0 times the thickness of the bottom of the bowl, the thickness of the cover of each of the lower bows is 1.0-1.5 times the thickness of the bottom of the uppermost bowl, and the conical orifices of all the parts that can be connected together form a smooth passage with an angle of taper of 10-20°, the diameter of the cone in its lower part being 3-5 mm.

6. Multicompartment container according to claim 4 or 5, wherein the heat-removing device forms a single unit with the bottom of the bowl and the cover of the next bowl down.

7. A method of making an UV region < 200 nm transmitting optical fluoride crystal for excimer laser lithography optics, said method comprising:
providing a multicompartment container for growing optical fluoride crystals, said multicompartment container having a number of graphite bowls placed on top of one another to form a stack and which have a central conical orifice in the bottom of each of them and a seeding unit that has a central cylindrical orifice and is arranged under the lower most bowl, and each bowl is fitted with a heat-removing device in the form of a graphite cylinder with a central conical orifice and is mounted under the bottom of each bowl and adjoins with its other surface the cover of the next bowl down, with the cover of each bowl except the uppermost bowl, having a central conical orifice, and progressively growing optical fluoride crystals in said bowls while minimizing radial gradients in the growing crystal and removing heat from the bottom of the bowl in an axial direction.

BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/09463

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C30B 35/00
US CL : 117/81, 83, 200, 204, 900

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 117/81, 83, 200, 204, 900

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
STN (HCAPLUS, JAPIO, INSPEC, USPATALL)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6, 375, 551 B1 (Darcangelo, et al) 23 April 2002, column1-9, lines 1-68, respectively.	1-7

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search

03 July 2002 (03.07.2002)

Date of mailing of the international search report

2 21 AUG 2002

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

Felisa Hiteshew

Telephone No. (703) 308-0661

Jean Proctor
Paralegal Specialist

Form PCT/ISA/210 (second sheet) (July 1998)